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Measurements of organic species in air and seawater from the tropical Atlantic

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[1] A West -East crossing of the Tropical Atlantic during Meteor cruise 55 included measurements of organic species within the atmospheric marine boundary layer and the upper ocean. Acetone, methanol, acetonitrile and DMS were measured between 10–0°N and 35°W–5°E, on either side of the ITCZ. Methanol and acetone concentrations were higher in the northern hemisphere, both in surface seawater and the atmosphere whereas acetonitrile and DMS showed no significant interhemispheric gradient. Three depth profiles from 0–200 m for these species were measured. Acetone, methanol, DMS and acetonitrile generally decreased with depth with the sharpest decrease in concentration in all profiles being found at the bottom of the mixed layer. The average air mixing ratios and surface seawater concentrations for the whole dataset are respectively: acetone 0.53 nmol/mol and 17.6 nmol/L; acetonitrile 0.11 nmol/mol and 6.19 nmol/L; methanol 0.89 nmol/mol and 118.4 nmol/L; and DMS 0.05 nmol/mol and 1.66 nmol/L. *INDEX TERMS:* 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1610 Global Change: Atmosphere (0315, 0325); 1635 Global Change: Oceans (4203); 4850 Oceanography: Biological and Chemical: Organic marine chemistry. **Citation:** Williams, J., R. Holzinger, V. Gros, X. Xu, E. Atlas, and D. W. R. Wallace (2004), Measurements of organic species in air and seawater from the tropical Atlantic, *Geophys. Res. Lett.*, *31*, L23S06, doi:10.1029/2004GL020012.

1. Introduction

[2] Recent studies have shown that organic species, in particular oxygenates, are more abundant in the atmosphere than previously thought [*Crutzen et al.*, 2000; *Singh et al.*, 2001], and play key roles in atmospheric chemistry, supplying reactive carbon, nitrogen and radicals to the remote troposphere, thereby influencing the global ozone budget [*Tie et al.*, 2003; *Folkins and Chatfield*, 2000]. However, large uncertainties exist in how the ocean influences the global atmospheric budgets of these species [*Galbally and Kirstine*, 2002; *Heikes et al.*, 2002; *Jacob et al.*, 2002], and how deposition of these atmospheric species influences surface ocean waters [*Duce and Liss*, 2002].

[3] The ocean-atmosphere interactions of selected organic species were investigated during Cruise 55 of the research ship Meteor to the tropical Atlantic (October–November 2002). On-board instrumentation was used to measure key organic species (including acetone, methanol, DMS and acetonitrile) in the atmosphere and ocean simultaneously. Additional species, including alkanes, organohalogens, CO and ozone were measured in the atmospheric marine boundary layer only (V. Gros et al., Tracing the origin of interlaced atmospheric pollution events over the Tropical Atlantic Ocean with satellites, trajectories, emission inventories and global models, submitted to *Journal of Geophysical Research*, 2004, hereinafter referred to as Gros et al., submitted manuscript, 2004). The ship steamed from Curacao (69°W) to Cameroon (9°E) approximately along 10°N, see Figure 1. The ship made two mid-Atlantic meridional transects (10°–0°N and 0°–10°N) crossing the Inter Tropical Conversion Zone (ITCZ) at about 5–6°N. Three depth profiles of acetone, methanol, DMS and acetonitrile were made between 0–200 m at locations P1–P3 in Figure 1.

2. Methods

[4] Two proton transfer mass spectrometers (PTR-MS) were employed to measure masses 33, 42, 59 and 63 which have been attributed to methanol, acetonitrile, acetone and DMS respectively. These identifications are in keeping with previous studies although minor contributions from other species, such as propanal to mass 59, cannot be ruled out [*Lindinger et al.*, 1998; *Williams et al.*, 2001]. Ambient air was drawn rapidly (ca. 100 L min^{-1}) from the bow, 18 m above the ocean, through a 1.91 cm diameter, ca. 20 m Teflon line. The inlet residence time was estimated as <5 seconds. A fraction of this flow was sampled by a PTR-MS located in an upperdeck laboratory. A clean marine pump (ECO ME- Meerestechnik-Elektronik, Trappenkamp, Germany) was used to continuously pump seawater from 5 m depth to a second PTR-MS instrument, located 3 m above sea level. To determine the variation of organic species as a function of depth, 10 L Niskin bottles were closed at preselected depths within a 24 bottle rosette steel sampler equipped with a conductivity-temperature-depth probe. The Niskin bottles had been specially constructed for sampling of low-levels of organic compounds, including use of Teflon-coated metal springs to avoid possible contamination.

[5] For both surface measurements and depth profiles a measured volume of seawater ca. 2 L was drawn into a glass vessel and sparged with helium at 1 sLpm for 25 minutes to purge the organics. A downstream cold trap (−150°C) collected the purged organic species. By flushing the trap with nitrogen and heating the trap, peaks were generated in

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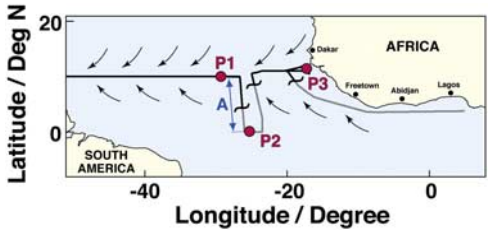

Figure 1. The cruise track is shown. Black arrows indicate the prevailing trade winds and the tildes indicate where the ITCZ was crossed. The letter A marks the north south section shown in Figure 3. P1 to P3 mark the positions of depth profiles plotted in Figure 4.

the monitored ions. These peaks were integrated to derive areas proportional to the seawater concentrations. Gas phase calibration was achieved using a commercial gas standard (Apel-Riemer Environmental Inc.) which compared closely to theoretically derived calibration factors [*Su and Chesnavich*, 1982]. For the seawater measurements, additional calibrations were performed by standard addition to seawater. The overall accuracy of the air measurements is estimated as within 20% and the seawater measurements within 30%. Measurements of nitrite and temperature made during these profiles were made with an autoanalyser and Seabird CTD probe according to standard methods.

[6] 2.4 L electropolished canisters were filled to 3 Bar with a metal bellows pump and subsequently analyzed by GC-MS for alkanes and organohalogens within three months of cruise end (Gros et al., submitted manuscript, 2004). Calibration was relative to a compressed ambient air sample, calibrated at NCAR to a NIST standard. The overall uncertainty for all quoted compounds was better than 15%. Ozone was measured using a UV absorption instrument (Thermal Environmental 49 and 49C) and was calibrated just before the campaign. The estimated accuracy is better than 5%.

3. Variation With Longitude and Latitude

[7] The atmospheric and seawater dataset for methanol, acetonitrile, DMS and acetone is shown as a function of time in Figure 2 and in overview in Table 1. In all cases, filled symbols represent hourly average gas phase mixing ratios and open symbols the individual seawater concentration measurements. Methanol, DMS and acetonitrile do not show a strong longitudinal dependency, in the atmosphere (NH, r = 0.2, r = 0.0, r = 0.3: SH, r = 0.3, r = 0.1, r = 0.3) or in the surface water (NH, r = 0.1, r = 0.1, r = 0.3,: SH, r = 0.3, r = −0.5, r = −0.1). The correlation of acetone with longitude is higher both in the air (NH r = 0.6: SH r = 0.5) and in the surface water of the northern hemisphere (NH r = 0.6: SH r = 0.3).

[8] When sailing directly south, along section A in Figure 1, the Meteor crossed the Inter-Tropical Convergence Zone (ITCZ) between 5–6°N. The air mixing ratio and surface seawater concentration for methanol, acetone, DMS, and acetonitrile from this transect are shown in Figure 3 with ozone and propane. The ITCZ is a barrier to mixing between the atmospheric hemispheres. Strong interhemispheric concentration gradients can develop for species that are short lived in comparison to the interhemispheric mixing time (1–2 years), or for species with uneven

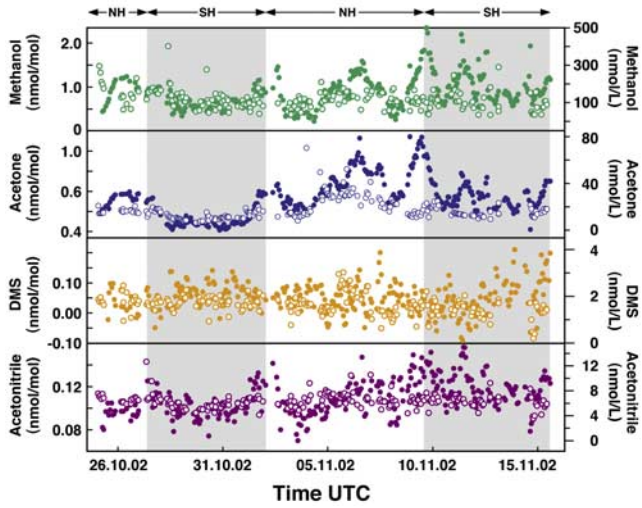

Figure 2. Air mixing ratios (solid circles) and surface water concentrations (open circles) are plotted as a function of time, see Figure 1. The southern hemispheric section marked in grey shading.

hemispheric source strengths. The sharp atmospheric concentration gradients between 5–6°N for propane, ozone, acetone, and methanol (lifetime between 1–3 weeks) all coincide closely with the meteorologically determined position of the ITCZ. No gradient was observed across the ITCZ in either surface seawater or in the atmosphere for DMS or acetonitrile although at the equator DMS seawater concentrations appear to increase and acetonitrile to decrease. The atmospheric lifetime for DMS (ca. 2 days) is so short that significant ambient levels are probably the result of local production and the slight increase in seawater DMS at the equator may be associated with the weak upwelling found in this region.

[9] Interestingly, surface seawater concentrations of methanol and acetone are closely correlated with the atmospheric mixing ratios across the ITCZ although the ITCZ is only a barrier to mixing in the atmosphere and not in the ocean. The similarity of the seawater concentration gradients to those in the atmosphere across the ITCZ, strongly suggests that uptake of acetone and methanol from the atmosphere determines the surface seawater concentrations measured in this region, at this time. The return leg (south-north) was affected by biomass burning (Gros et al., submitted manuscript, 2004) and hence not considered representative of the background case.

4. Depth Profiles

[10] Three depth profiles for the organic species were taken at the positions marked as P1–P3 in Figure 1. Figure 4

Table 1. Average, Median, and Standard Deviations for Air and Seawater Measurements

	Air (nmol/mol)				Sea (nmol/L)			
	Ave.	σ	Med.	n	Ave.	σ	Med.	n
Methanol	0.89	0.40	0.87	500	118.4	48.2	114.1	210
Acetonitrile	0.11	0.02	0.12	502	6.2	1.1	6.2	192
Acetone	0.53	0.20	0.52	503	17.6	8.1	15.2	213
DMS	0.05	0.05	0.05	507	1.7	0.4	1.6	214

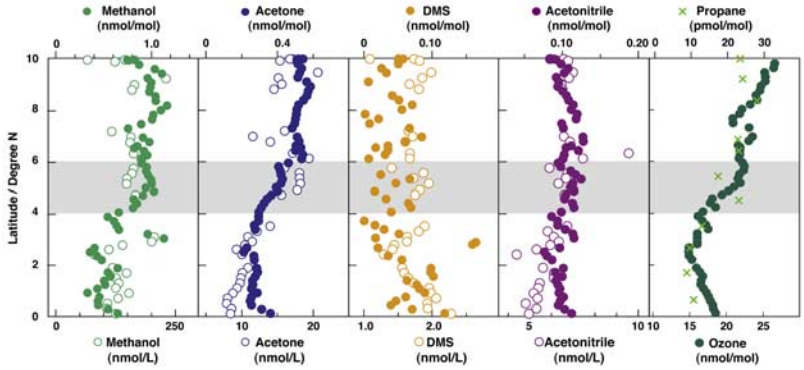

Figure 3. Selected air mixing ratios (solid circles and crosses) and surface water concentrations (open circles) are plotted as a function of latitude along section A shown in Figure 1. The position of the ITCZ is shown in grey shading.

shows the depth profiles of the organic species methanol, acetone, acetonitrile and DMS with temperature and nitrite data. The seawater concentration of the organics are generally higher in the surface waters than at 150–200 m. The maximum rate of decrease as a function of depth for all species is coincident with the bottom of the mixed layer which is also marked by a nitrite maximum. This marks the division between relatively well-mixed surface waters, where seawater temperature remains constant due to close contact with the atmosphere, and the stratified, deeper ocean where contact with the atmosphere is indirect (via diapycnal mixing and lateral processes).

5. Transatlantic Flux Measurements

[11] Ocean-atmosphere fluxes of acetone, methanol, acetonitrile and DMS have been calculated based on air and surface seawater measurements with the simple sea to air flux model (equation (1)).

$$F = k(C_w - H^*C_a) \quad (1)$$

The flux F is determined by: the transfer velocity, k, the aqueous phase concentration, C_w, the concentration in the gas phase, C_a, and the Henrys law coefficient, H, which is defined as $H = C_w/C_a$ at equilibrium. The transfer coefficient k was calculated according to the parameterisation of *Wanninkhof* [1992]:

$$k = 0.39*u^{2}*\mathrm{sqrt}(660/Sc)$$

[12] The transfer coefficient (k) depends on the wind speed normalised to 10 m above the ocean (u) and the Schmitt number (Sc = v/D), which in turn depends on the kinematic viscosity of seawater (v) and the diffusion coefficient of the gas in seawater (D). The diffusion coefficients were calculated as a function of measured salinity and water temperature according to *Hayduk and Laudie* [1974].

[13] The median flux of DMS 2.5 μmol/m^2/day, (ave = 3.6, σ = 3.7, n = 197) is positive, indicating emission from the ocean, and is comparable to those in the literature [*Kettle et al.*, 2001]. The median fluxes of acetonitrile 1.6 μmol/m^2/day (ave = 2.6, σ = 3.3, n = 192) and acetone 8.5 μmol/m^2/day (ave = 11.7 σ = 15.4, n = 199) also indicate emissions, whereas the negative flux of methanol −33.7 μmol/m^2/day (ave = −66.2, σ = 266.5, n = 195) indicates a variable uptake from the air to the sea.

6. Discussion

[14] The atmospheric measurements presented here are generally consistent with previously reported measurements at similar latitudes, in unpolluted conditions, with similar instrumentation [*Crutzen et al.*, 2000], and significantly lower than those made in polluted East European outflow [*Salisbury et al.*, 2003]. Seawater data for species other than DMS is sparse. We know of no previous measurements of methanol with which to compare these values. However the data presented here is at the lower end of the range (0.1–0.6 μM) predicted by a global model [*Galbally and*

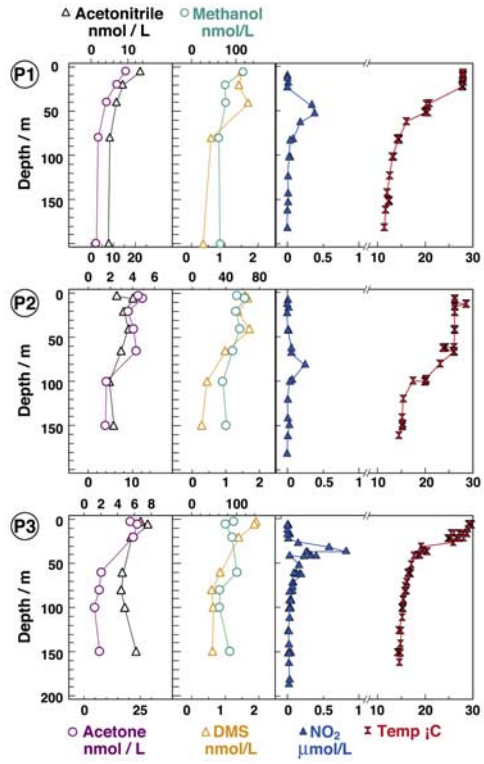

Figure 4. Depth profiles for acetone, acetonitrile, DMS and methanol with temperature and nitrite.

Kirstine, 2002] and to those predicted by an air sea exchange model constrained with atmospheric measurements (0.1 μM) [*Singh et al.*, 2003] (*Singh et al.* [2003] refers to an incorrect preliminary version of this seawater dataset shown on a poster EGU 2003). To our knowledge there are no previous seawater measurements of acetonitrile reported from the open ocean. Similar nano to pico molar concentrations of a number of carbonyl compounds including acetone have been reported in both surface waters and as a function of depth [*Kieber and Mopper*, 1990; *Zhou and Mopper*, 1997].

[15] From this data we may compare the burden of these species in the surface ocean mixed layer (0–50 m) to the total tropospheric burden. Assuming a surface ocean volume of 1.81×10^{19} L, a tropospheric mass of 4.63×10^{21}g, and a uniform global distribution we calculate from median values that the oceanic burdens of acetone, acetonitrile and methanol would be 15.9 Tg, 4.6 Tg and 66.1 Tg whereas tropospheric burdens would be 4.8 Tg, 0.79 Tg, 4.5 Tg, respectively. The surface ocean therefore appears to contain much more of these species than the troposphere and hence is a significant reservoir, as suggested previously by *Galbally and Kirstine* [2002] and *Singh et al.* [2003]. The measurements presented here support these earlier hypotheses.

[16] Highly variable fluxes can be expected in this region since the atmosphere overlying the Tropical Atlantic ocean is sequentially exposed to the effects of biomass burning, anthropogenic emissions and, as the ITCZ migrates, air from both hemispheres. The median fluxes given represent only a snapshot of the situation during this cruise and should not be considered as a global average flux strength. The calculated flux for methanol is negative indicating uptake by the ocean. This is consistent with the trend observed across the ITCZ and the depth profiles. In the case of acetone, the positive median flux calculated for this campaign appears to contradict the trend across the ITCZ. The predicted positive flux for acetonitrile is also surprising since previous measurements have exclusively suggested a sink [*Bange and Williams*, 2000; *Warneke and de Gouw*, 2001]. The explanation for these anomalies may partly lie in the time of year that this cruise took place. In October and November, as biomass burning emissions of methanol, acetone and acetonitrile recede, surface water supersaturations can give regions of positive flux from the ocean to the air.

[17] All four organics reported here generally decrease with depth between 0 and 200 m. The vertical gradients are most pronounced for acetone and DMS. The strong decrease of DMS with depth, is known to reflect a balance between phytoplankton-associated production that is strongest in the sunlit surface layer and microbial degradation that is less strongly depth-dependent [*Kiene and Bates*, 1990]. The processes that determine the profiles of methanol, acetone and acetonitrile are less well understood. The relative ratio between surface layer and sub-surface (150–200 m) concentrations is ~5 for DMS and acetone, and only 1–2 for acetonitrile and methanol. If we assume that all of these compounds share, in common with DMS, an exclusively near-surface source (e.g., phytoplankton-associated production or uptake from the atmosphere) then one could infer from the profile shapes that acetone degradation rates are quite rapid (comparable to those for DMS), and that the sub-surface lifetimes of methanol and acetonitrile are significantly longer. If our estimation of net emission of acetone from the ocean is both correct and applicable to larger spatial/temporal scales, then a short sub-surface lifetime for acetone would imply a near-surface production pathway for this compound (as for DMS). For the other compounds, the less-steep vertical profiles might reflect slower degradation or, alternatively, sub-surface production pathways associated with microbial processes or from HO initiated seawater chemistry from nitrite photolysis [*Qian et al.*, 2001].

[18] A number of potentially important links between the atmosphere and the ocean for organic species are highlighted here. It is hoped that the new SOLAS initiative [*Duce and Liss*, 2002] will stimulate the measurements required for better a understanding the role of ocean-atmosphere exchange on global atmospheric chemistry.

[19] **Acknowledgments.** We thank Meteor crew for their able assistance and Dieter Scharffe for installation. The logistical help of Hermann Bange is gratefully acknowledged as is Verity Stroud for NMHC analyses. NCAR is operated by the University Corporation for Atmospheric Research under sponsorship of the National Science Foundation. This work was funded by the DFG (Grants WA 1434/3 and grant WI 2130/1-1).

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